Laser Original**Reactor Utilization Factor in Laser Isotope Separation****Kazuo TAKEUCHI* and Kei SUNOUCHI****

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A method is presented for the quantitative evaluation of the reactor utilization factor for laser isotope separation, in a compartments-in-series type reactor in which a laser beam is focused at the center of each compartment. We show that the maximum process flow rate for this reactor is obtained as the product of this factor with the flow rate for an ideal reactor that uses a parallel beam. An example of the evaluation of this factor is given for a CTF₃/CHF₃ system.

Key Words: Laser Isotope Separation, Optimization, Reactor Utilization Factor.

1. Introduction

In a previous paper we reported that CTF₃ was dissociated selectively with a monochromatic pulsed CO₂ laser beam and TF was formed as the photoproduct. As the separation of hydrogen fluoride (TF/HF) from trifluoromethane (CTF₃/CHF₃) is much easier than the isotopic separation of CTF₃ from CHF₃, the selectivity of the laser-induced reaction is the main issue in laser isotope separation. To estimate and design the laser isotope separation process, we first showed the way to extract useful relations called dissociation characteristics from small scale experiments^{1,2)}. Second, we surveyed possible working substances³⁻⁶⁾, and obtained the data through this procedure. Using these data, next, we showed the attainable flow rate of the working substance for unit average laser power for the case with the ideal reactor in which the laser energy is fully used⁷⁾. But, in practice, the laser beam

has to be focused to avoid damage to the windows. This reduces the factor of reactor utilization to less than unity. In our proposed reactor for laser isotope separation of tritium⁸⁾, the laser beam was sequentially focused in compartments connected in series with lenses that also served as the beam entrances. In this way, the laser fluence necessary for isotopically selective dissociation was attained at the center of each cell, while the lens windows were left undamaged. The laser pulse energy decreased in the direction of the beam propagation owing to the beam absorption in each compartment and reflection losses at the lenses. The focal lengths of the lenses were sequentially reduced so as to maintain the focal fluences at a constant level. The reactant CTF₃/CHF₃ gas was made to flow continuously in the reactor, and some of it was converted to the product TF/HF after being exposed to the laser beam. One of the advantages of this reactor is that the residence time distribution of the reactant gas improves with increasing number of compartments in the same way as con-

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Fig.1 Schematic diagrams of focused and parallel beam experiments. a) axial profile of Φ in the focused beam experiment; b) beam envelope of the focused beam experiment; focal volume is shown with broken lines; c) axial profile of q in a focused beam experiment, d) axial profile of q in hypothetical cylinder (length $2l$); e) axial profile of Φ in the parallel beam experiment; f) beam envelope of the parallel beam experiment; g) axial profile of q in parallel beam experiment; h) transverse profile of Φ ; i) transverse profile of q .

ventional reactors of this type⁹⁾. Nevertheless, as an inevitable consequence of the beam focusing, the reactor suffers from the disadvantage of deterioration in photon utilization. Namely, when the beam is focused as shown in Fig.1-b, the gas near the window absorbs the laser energy, while the yield of the dissociated CTF_3 is low here because of the low fluence. Thus, the laser energy is not effectively dissociate CTF_3 near the windows. In this paper, this disadvantage of focusing is quantitatively evaluated as functions of the parameters characteristic of the materials. We demonstrate that this reactor utilization factor has to be taken into account to discuss the process capabilities of the working molecules.

2. Mathematical Model

Let Φ_f and Φ_c denote the focal fluence and the critical fluence, respectively. Φ_c is the minimum fluence to yield reaction saturation. It is one of the two parameters to describe the dissociation characteristics, which will be discussed later in more details with Eqs. 3-a and 3-b. We suggested in a preceding paper¹⁾ that the dimensionless focal fluence, Φ_f / Φ_c , in the reactor has an optimum value to maximize the volume of reaction. As the optimum focusing is a function of Φ_f / Φ_c and not of pulse energy, we can optimize the performance of the whole reactor by optimizing the focusing in each compartment,

irrespective of the decreasing pulse energy in the direction of the beam propagation. Therefore, optimization for one compartment is sufficient for further discussion.

Consider the reactor utilization in the i -th compartment for the focused beam (Fig.1-b with the focal radius of r_f) compared with that for the unfocused (parallel) beam (Fig.1-f) with the beam radius set equal to r_f . When the envelope of the focused beam is assumed to be hyperbolic, the beam radius at the window r_w is given by²⁾

$$r_w^2 = r_f^2 \left\{ 1 + \left(\frac{L_i}{a_i} \right)^2 \right\} \quad (1)$$

where r_f , L_i and a_i are the radius at the focal point, half cell length, and the length of the confocal region, respectively. We assume the transverse profile of the fluence (B-B' in Fig.1-b) is uniform as shown in Fig.1-h, while the axial profile of Φ has a maximum (Fig.1-a). The reaction volume V_R is the volume of the resonant reactant (such as CTF₃) dissociated by one laser pulse, and is given by

$$V_R = \int_V q dV \quad (2)$$

where q is the reaction probability per pulse and V is the reactor volume. The dependence of q on Φ is called the dissociation characteristics. In our model, the value of q is related to the local fluence Φ with two parameters Φ_c and n as

$$q = (\Phi/\Phi_c)^n \quad (\text{for } \Phi \leq \Phi_c) \quad (3-a)$$

$$q = 1 \quad (\text{for } \Phi > \Phi_c) \quad (3-b)$$

The parameter n , which is dependent on gas pressure, is found usually between 3 and 6. In our previous work¹⁾, such assumption was found sufficiently accurate. According to the model we developed for the focused beam geometry⁹⁾, the dimensionless reaction volume Y ($\equiv V_R/V_f$) is related to the dimensionless focal fluence F ($\equiv \Phi_f/\Phi_c$) in the following form:

$$Y = \Theta F^n \quad (\text{for } F \leq 1) \quad (4)$$

where V_f is defined as the focal volume ($\equiv 2\pi r_f^2 a$) and Θ is a constant given numerically as a function of n as shown elsewhere²⁾. The value of Θ is relatively insensitive to n : Θ changes from 0.79 to 0.43 when n is increased from 3 to 6. Let E_i and ΔE denote the pulse energy at the focal point and the absorption loss between the window and the focal point, respectively. Then, the following relations hold:

$$E_i + \Delta E = \Phi_w \pi r_w^2 = \Phi_w \pi r_f^2 (1 + L_i^2/a_i^2) \quad (\text{at the window}) \quad (5)$$

$$E_i = \Phi_i \pi r_f^2 \quad (\text{at the focal point of the } i\text{-th compartment}) \quad (6)$$

where Φ_w is the acceptable beam fluence at the window. In practice, the value of Φ_w may be set slightly less than the actual damage threshold fluence of the window material. When the number of the compartments is fairly large, say 10 for example, the decay of the pulse energy within one compartment is small. Then, the pulse energy in i -th compartment may be approximated as constant, and taken as E_i . As the number of compartments increases, ΔE approaches zero. By combining Eqs. (5) and (6) and assuming $\Delta E \ll E_i$, we obtain following:

$$L_i/a_i = (\Phi_i/\Phi_w - 1)^{1/2} \quad (7)$$

The reaction volume in a focused beam experiment is obtained by integrating the non-uniform q over the entire cell. Figure 1-c shows such a case where the maximum q is less than unity. Instead of this non-uniform reaction zone, we consider a cylindrical reaction zone of radius r_f , of length $2l$ with a constant q . The value of l is so determined that its reaction volume (hatched zone in Fig.1-b) becomes equal to V_R . Therefore, generally speaking, l is not equal to

a. In this hypothetical cylinder, the reaction probability is uniformly set equal to q_f , the value of the reaction probability at the focal point in focused beam geometry (see Fig.1-d). From the definitions of Y and l , we obtain

$$V_{Ri} = 2\pi r_f^2 a_i Y = \pi r_f^2 (2l_i) q \quad (8)$$

$$\text{or, } a_i Y = q l_i. \quad (9)$$

For comparison, a parallel beam experiment to yield the same reaction probability is shown in Fig.1-f. The corresponding axial profiles of Φ and q are shown in Figs.1-e and 1-g, respectively. The transverse profiles of Φ and q for both the focused beam geometry (Fig.1-b) and the parallel beam geometry are shown in Figs.1-h and 1-i, respectively. The parallel beam geometry with a radius r_f would be possible if the value of Φ_w could be increased as high as Φ_f . Now, the reactor utilization factor η for the focused η beam geometry is obtained as the ratio of the reaction volumes for the uniform dissociation probabilities of Fig.1-d and Fig.1-g. Since the cross sectional areas of the hypothetical cylinder in Fig.1-b and of the cylinder in Fig.1-f are identical, the reactor utilization factor η is the ratio of the reaction lengths:

$$\eta \equiv l/L \quad (10)$$

We assume that saturation ($q=1$) does not occur in our focused beam geometry. Using Eqs. (7), (9), (3-a) and (2), we rewrite Eq. (10) as

$$\begin{aligned} \eta &= \left(\frac{Y}{q} \right) \frac{1}{\{(\Phi_f/\Phi_w) - 1\}^{1/2}} \\ &= \frac{\Theta}{\{(\Phi_f/\Phi_w) - 1\}^{1/2}} \end{aligned} \quad (11)$$

This final relation expresses the reactor utilization factor in generalized form as a function of Φ_f , Φ_w and Θ .

For the case of $F > 1$, η can also be expressed

Fig.2 Schematic illustration of the dependence of η on (Φ_w / Φ_f) . The solid line is realistic, and the broken line is an approximation (see Eq. (11) and text).

as a function of these parameters but in a more complex form that will not be discussed here. It should be noted that Eq. (11) is only valid for $\Phi_f \gg \Phi_w$. It is erroneous to apply Eq. (11) to the case with $\Phi_f \sim \Phi_w$; η approaches unity in the real situation, although naive use of Eq. (11) may suggest $\eta \rightarrow \infty$ as Φ_w approaches Φ_f . This limitation is illustrated schematically in Fig.2 where the solid and broken curves represent the actual and predicted dependency; Equation (11) is a good approximation only for $\Phi_w / \Phi_f < 0.5$. The limitation of Eq. (11) originates in an assumption in the derivation of Eq. (4), namely that no reaction occurs near the window. This is true for all the focused-beam experiments using $\text{CTF}_3/\text{CHF}_3$, but not necessarily so for low Φ_c substances such as $\text{C}_4\text{TF}_9^{(3)}$.

3. Numerical Example

In the preceding paper⁷⁾, we reported the contour maps of photon utilization in laser isotope separation of tritium. In those maps, the quo-

Fig.3 Attainable process flow rate for a 1 kW average power laser for parallel beam reactor (-78°C , 9R (14) line of a CO_2 laser): q/ϵ_{abs} (in $\text{mol}\cdot\text{s}^{-1}\cdot\text{kW}^{-1}$ unit) as a function of total pressure P and fluence Φ .

tient of the reaction probability per pulse for CTF_3 , q , and the absorbed energy ϵ_{abs} per unit mole of the reactant for given laser conditions, q/ϵ_{abs} , were chosen as the objective function, and the fluence and the total pressure of the reactant were chosen as the control variables. Figure 3 is a reproduction from Reference 6 for one such contour map. The unit for q/ϵ_{abs} is $\text{mol}\cdot\text{s}^{-1}\cdot\text{kW}^{-1}$. When the selectivity of reaction is sufficiently high, and when the content of tritium is extremely low, the value of q/ϵ_{abs} gives the flow rate of the feed mixture ($\text{CTF}_3/\text{CHF}_3$) in (mol/s) unit attainable for 1 kW laser average power⁷⁾. It corresponds to the process capability. This map indicates that, theoretically, a feed rate as high as 0.2 mol/s can be attained at the total pressure of 10 kPa for a 1 kW laser. It is, however, not possible in practice to design a parallel beam reactor for the constant fluence of $100\text{J}/\text{cm}^2$ required in this case, as the damage threshold of the window

Fig.4 Attainable process flow rate for a 1 kW average power laser for focused beam reactor (same conditions as in Fig.3): $\eta q/\epsilon_{\text{abs}}$ (in $\text{mol}\cdot\text{s}^{-1}\cdot\text{kW}^{-1}$ unit) as a function of total pressure P and focal fluence Φ_f .

material is typically $3\sim 6\text{J}/\text{cm}^2$. For such a case, the photoreactor of the compartments in series as shown by our group⁸⁾ becomes one possible answer.

For Φ_w set equal to $2\text{J}/\text{cm}^2$, the contour map was recalculated by multiplying the contour height by η . The process flow rate in a practical reactor, $\eta q/\epsilon_{\text{abs}}$, is shown in Fig.4 as a function of total pressure P and of the focal fluence Φ_f . The peak height of the contour in Fig.4 is reduced by a factor of 6 compared with that in Fig.3. At the same time, the optimum pressure P is lowered and the optimum focal fluence is increased because η is a function of Φ_f and Θ as shown in Eq. (11) for given value of Φ_w . Note that Θ depends on P since Θ is a function of $n^{(1)}$ which depends on P .

4. Discussion and Conclusion

We show, first, how to utilize η and the contour maps for process evaluation. Suppose our

objective is to eliminate tritium from the waste water of a reprocessing plant. With sufficiently high separation factor (e.g. 10^4 as proved for $\text{CTF}_3/\text{CHF}_3$) and very low content of tritium (such as 1 ppm), we learn from Fig.4 that the molar flow rate of $\text{CTF}_3/\text{CHF}_3$ of 0.035 mol/s can be attained for 1 kW average laser power. Knowing the isotopic exchange process prior to laser irradiation requires roughly equimolar flow rates for both tritiated water and $\text{CTF}_3/\text{CHF}_3$, we can estimate the size of the laser required for given objective at optimum Φ_f and P . For example, to process 1000 ton of tritiated water every year (300 days in operation), or equivalently to process $\text{CTF}_3/\text{CHF}_3$ mixture at 2.1 mol/s, we need a laser with average power of $(2.1/0.035) = 60$ kW. This calculation is based on $\Phi_w = 2 \text{ J/cm}^2$.

In laser isotope separation of tritium, there are two groups of promising working substances. The first one is trifluoromethane, which has the highest q/ϵ_{abs} among the substances we surveyed⁷⁾. The disadvantage of this substance is the high Φ_c value typically $60 \sim 80 \text{ J/cm}^2$, compared with the typically acceptable fluence at the window Φ_w of $\sim 2 \text{ J/cm}^2$. The typical values of q/ϵ_{abs} and η are $0.2 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kW}^{-1}$ and 0.1, respectively. The second group consists of the substances such as $\text{CF}_3\text{CTClF}^{4)}$, $\text{CF}_3\text{CTBrF}^{5)}$ and $\text{C}_3\text{TF}_7^{6)}$, that have very low values for Φ_c , typically $4 \sim 10 \text{ J/cm}^2$, and also have a relatively low q/ϵ_{abs} value at the optimum condition. The typical values for q/ϵ_{abs} and η are $0.04 \text{ mol} \cdot \text{s}^{-1} \cdot \text{kW}^{-1}$ and 0.4, respectively. Although it is not our objective here to draw a conclusion with respect to the choice of the most suitable working

substance, it is appropriate to say that a comparison of the contour heights such as shown in Fig.4 is required to estimate the process capability. The first group may have a higher peak in the map for the ideal process flow rate (as in Fig.3), but η may be low compared with that for the second group, and vice versa. The calculation of $\eta q/\epsilon_{\text{abs}}$ instead of just q/ϵ_{abs} provides an equal basis for comparing the two groups of working substances.

Equation (11) for η also suggests that the development of a window material with high Φ_w is important for increasing η and the process flow rate of the feed for a given average laser power. For example, if we can have a window material with $\Phi = 20 \text{ J/cm}^2$ instead of 2 J/cm^2 , the value of η will be increased roughly three fold. Thus, the average laser power required for the same objective will be reduced to $1/3$.

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